Recent Progress in Surface Hopping: 2011−2015
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ABSTRACT: Developed 25 years ago, Tully’s fewest switches surface hopping (FSSH) has proven to be the most popular approach for simulating quantum-classical dynamics in a broad variety of systems, ranging from the gas phase, to the liquid and solid phases, to biological and nanoscale materials. FSSH is widely adopted as the fundamental platform to introduce modifications as needed. Significant progress has been made recently to enhance the accuracy and efficiency of the surface hopping technique. Various limitations of the standard FSSH—associated with quantum nuclear effects, interference and decoherence, trivial or “unavoided” crossings, superexchange, and representation dependence—have been lifted. These advances are needed to allow one to treat many important phenomena in chemistry, physics, materials, and related disciplines. Examples include charge transport in extended systems such as organic solids, singlet fission in molecular aggregates, Auger-type exciton multiplication, recombination and relaxation in quantum dots and other nanoscale materials, Auger-assisted charge transfer, nonradiative luminescence quenching, and electron− hole recombination. This Perspective summarizes recent advances in the surface hopping formulation of nonadiabatic dynamics and provides an outlook on the future of surface hopping.

M any important phenomena in physics, chemistry, biology, and material sciences can be approximated by representing the dynamics of a few key quantum particles, such as mobile charges or excitons, in a medium of an enormous number of classical degrees of freedom, typically nuclei. Examples include electron transfer,1,2 charge transport,3,4 and exciton relaxation,5,6 migration,7,8 fission,9,10 dissociation,11,12 and recombination.13,14 Because a purely quantum description of such large systems is too complex and time-consuming, and classical molecular dynamics completely lacks the ability to characterize essential quantum effects, mixed quantum-classical dynamics (MQCD) methods have become the most appropriate approach to simulate these ubiquitous charge and exciton dynamics.15,16 The primary and one of the simplest MQCD techniques is the mean field, or Ehrenfest, method.17,18 In this approach, the classical subsystem moves on a single potential energy surface (PES), which is averaged over all quantum states and weighted by the corresponding populations. The mean field approximation, however, is not always adequate. In general, it is valid when the quantum and classical parts are weakly coupled, or when nuclei react similarly to different quantum states.19

The concept of surface hopping has been proposed20,21 to deal with more complex situations. The major difference between mean field and surface hopping is that the latter introduces stochastic hops between PESs. Namely, the potential energy for nuclear dynamics changes discontinuously from time to time. The standard algorithm is Tully’s fewest switches surface hopping (FSSH),22 which is designed to minimize the number of state switches. After the system status—including the coordinates and momenta of the classical degrees of freedom, the wave function of the quantum particles, and the active surface—is initialized, the surface hopping algorithm is carried out in several key steps (Figure 1). For each time step, the classical particles evolve on the active PES according to the Newton equation, and the quantum parts are propagated through the time-dependent Schrödinger
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The advantage of surface hopping is enormous. Surface hopping algorithms are well-defined and straightforward to implement. They are normally benchmarked against exact quantum mechanical standard in carefully chosen models and, thus, have satisfactory computational accuracy. In general, 1000 trajectories are already enough to exhibit good statistics in surface hopping simulations. More trajectories or special algorithms may be needed to sample rare events. In practice, in application to large systems, tens of trajectories can already provide valuable insights into systems’ dynamics. The surface hopping probabilities obey approximately internal consistency, which means that the portion of trajectories on a given state at any time equals to the corresponding quantum population obtained by TDSE. Note that exact internal consistency can only be achieved using coupled trajectories. The energy conservation procedure makes surface hopping capable of approximately reproducing the Boltzmann distribution of the quantum states, which is important for accurate description of relaxation to thermal equilibrium and other thermodynamic properties. In comparison, the mean field approximation lacks this important feature. By design, the surface hopping trajectories are completely independent of each other, and thus, they can be handled efficiently with parallel computing. Surface hopping is fully compatible with modern electronic structure methods and, therefore, it can be used to explore complex dynamics in realistic systems at a first-principles level. In recent years, time-dependent density functional theory (TDDFT) has been combined with surface hopping and applied to a broad range of organic and inorganic materials undergoing charge separation, electron and energy transfer, energy relaxation, charge recombination, chemical reactions, and other nonequilibrium processes. Surface hopping can properly describe the nuclear reorganization effect, which is key for nonequilibrium dynamics, such as hopping transport of charge carriers in organics. Because of these advantages, the surface hopping technique, especially the standard FSSH, has retained its enormous popularity in chemistry, physics, biology, materials, and related disciplines in the past two and a half decades.

The great successes of FSSH encourage researchers to apply the technique to new systems and processes. In turn, novel applications reveal limitations of the standard FSSH. In general, all four steps of the standard surface hopping technique may cause problems (Figure 1). First of all, surface hopping is intrinsically limited by the assumption that classical mechanics provides an adequate description of the nuclear motion. Then it is straightforward to argue that the nuclear quantum effects, such as tunneling and zero-point energy, which are important for low temperature dynamics, are completely missing. Besides, the wave function in each realization of surface hopping is propagated with TDSE along its own trajectory. The lack of communication between evolving trajectories causes an excessive preservation of quantum coherences, making FSSH overcoherent. Quantum interference between two or more pathways requires proper treatment of coherence, and thus, it cannot be properly described by FSSH, especially at low energies. In addition, surface hops rely on the calculation of NA couplings between adiabatic states. In large systems with a high density of electronic states, there exist many situations in which the states are weakly coupled and are localized in spatially different parts of the system. This situation leads to a huge number of trivial crossings, in which the NA couplings behave as delta functions of time. Accurate calculations require very small time steps, and thus are extremely time-consuming. Further, because total electron–nuclear energy is conserved in FSSH, certain phenomena, for example, the superexchange mechanism of population transfer, are prohibited. Here, a singlet excitation converts to a triplet pair by coupling through virtual charge transfer states, and thus, the number of electron–hole pairs can be potentially doubled for photovoltaics applications. Auger phenomena also proceed via a two-particle superexchange type of mechanism. Auger processes are very common in nanoscale materials; for instance, they contribute to fast electron energy losses and multiple exciton generation in colloidal quantum dots. Finally, although TDSE for wave function propagation is representation independent, FSSH results can depend strongly on the representation used, which is against standard quantum mechanics. In particular, the dependence arises because the velocity adjustment process differs strongly in diabatic and adiabatic representations. Because of its extreme simplicity and an enormous success, FSSH is adopted as a platform to introduce corrections and modifications as needed. Recent years have witnessed substantial progress along this direction to resolve the various limitations of the surface hopping formulation of NA quantum dynamics. In this Perspective, we summarize the latest progress in the development of more efficient and accurate FSSH-like surface hopping strategies developed within the last five years, including ring-polymer surface hopping (RPSH), phase-corrected FSSH (PC-FSSH), semiclassical Monte Carlo (SCMC), augmented-FSSH (A-FSSH), coherence penalty functional (CPF), the Min-Cost algorithm, flexible surface hopping (FSSH), self-consistent FSSH (SC-FSSH), Markov state surface hopping (MSSH), global flux surface hopping (GFSH), Liouville space FSSH (LS-FSSH) and GFSH (LS-GFSH), decoherence-induced surface hopping (DISH), and second-quantized surface hopping (SQUASH). We also offer an outlook on future research needs in this field.
expressed as a linear combination of a set of orthogonal basis states in Hilbert space, \( \{|i\rangle\} \)
\[
|\psi(t)\rangle = \sum_i c_i(t)|i\rangle
\]  
(1)
The time evolution follows the TDSE
\[
\frac{d|\psi(t)\rangle}{dt} = \frac{i}{\hbar}\hat{H}|\psi(t)\rangle
\]
(2)
where \( \hat{H} \) is the system Hamiltonian. Substituting eq 1 to eq 2 and projecting the result onto electronic basis states, we have
\[
\frac{dc_k}{dt} = \frac{1}{i\hbar} \sum_j c_j(H - i\hbar \nu \cdot d)_{kj}
\]
(3)
where \( H_{ij} = \langle k|i\rangle \) and \( (\nu \cdot d)_{kj} = \langle k|\frac{d}{dt}|j\rangle \) are diabatic and NA couplings, respectively. The NA couplings are the driving force for the ring polymer becomes significant. At low temperature, however, the spatial extent of the centroid approximation, especially in the low temperature regime, where nuclear tunneling is most important. The RPMD is closely related to centroid molecular dynamics.57

**Interference and Decoherence.** Wave functions in quantum mechanics evolve into superposition of basis states. Quantum superpositions give rise to interference effects. Coupled to a quantum mechanical environment, that is, a bath, the system undergoes a nonunitary evolution, and superpositions lose coherence, that is, decohere. Because the vibrational bath is classical in FSSH, the system’s evolution is unitary, and decoherence is excluded at the level of individual trajectories. This may lead to huge errors in quantum transition rates. The limit of infinitely fast decoherence gives rise to the quantum Zeno effect,59 when quantum dynamics stops completely. The term “decoherence” is closely related to “pure-dephasing” in the optical response theory.60 Decoherence can be viewed as the time-domain version of the Franck-Condon overlap in the energy domain.60

Multiple approaches have been proposed in recent years to deal with quantum interference and decoherence within surface hopping. It is possible to model decoherence as phase randomization obtained by averaging over an ensemble of systems undergoing unitary evolution in the presence of a classical bath. FSSH utilizes a single nuclear trajectory to solve the TDSE for the electronic wave function. In contrast, the nuclear wave packet in a fully quantum electron–nuclear description splits into several branches correlated with different electronic states. The paths of the different branches of the nuclear wave packet can be roughly identical only in the limit of a high nuclear momentum. In most situations, different parts of the nuclear wave function move at different velocities, and contribute different phases to the overall wave function. To resolve this inconsistency, the phase corrected FSSH (PC-FSSH) method has been suggested.61 In a representative two level model, the nuclear wave function is assumed to be a linear combination of two Gaussian wave packets which are placed on two electronic adiabats. At time zero, the two Gaussians locate at the same position with the same phase but with different momenta \( (p_1 \) and \( p_2) \). The momentum difference arises due to differences in the kinetic energies of the wave packets moving on different adiabats. The phase difference between states 1 and 2 at time \( t \) is found to be \( \exp \left[ \frac{i}{\hbar} \int_{0}^{t} \left( \hat{p}_1 - \hat{p}_2 \right) \right] \) with \( \hbar \) being the mass of the particle.62 To realize the phase correction, one simply uses a modified electronic Hamiltonian to propagate the wave function, without altering any other machinery of the standard surface hopping algorithm. Namely, one uses \( -\hat{p}_1 \cdot \hat{p}_2 / m (\text{or} -\hat{p}_2 \cdot \hat{p}_1 / m) \) and \( -\hat{p}_1 \cdot \hat{p}_2/m \) to replace the corresponding diagonal elements of the electronic Hamiltonian. In this way, the nuclear momenta are directly related to the phase evolution of the electronic wave function, agreeing with quantum mechanics. This simple correction adds almost no computational cost to the algorithm but leads to a dramatic improvement when treating scattering probabilities in one- and two-dimensional dual avoided crossing models with strong interference effects (see Figure 2).62 Note that PC-FSSH with slight modifications can introduce partial decoherence to surface hopping.62
The Wentzel–Kramers–Brillouin approximation gives general solutions to linear differential equations such as the TDSE. It is widely adopted to build semiclassical descriptions of quantum mechanics.62 Recently, this approximation has been combined with the path integral formalism to generate the semiclassical Monte Carlo (SCMC) algorithm for NA dynamics.47 The realization of SCMC consists of two major steps. The preprocessing step is similar to the traditional surface hopping schemes. A swarm of classical trajectories are propagated on-the-fly, whereas surface hops are allowed and energy is strictly preserved. The accumulated phase information associated with each classical trajectory is further used to perform the postprocessing evaluation of the multidimensional path integral series using the Monte Carlo sampling of classical trajectories. The trajectories are sorted out into groups based on their final electronic states and the number of hops that have occurred. Each group represents a sample that is used to evaluate the corresponding integral to get the total probability for the electron to occupy each state. Similar to the common surface hopping approaches, SCMC can be combined naturally with an arbitrary electronic structure theory method. The construction of SCMC is not ad hoc. It is able to account for both quantum interference (see Figure 2) and decoherence effects.47

Decoherence gives rise to collapse of the wave function to pure states.35 This could be achieved with discontinuous19,32,63,64 or continuous46,49,54,65,66 strategies, both of which have been developed in recent years. The discontinuous approach collapses the wave function stochastically based on the decoherence time32,63 or the displacement away from the NA regime.19,64 Within this strategy, the MQCD undergoes stochastic events because of hops or collapses, which accounts for wave packets on different surfaces exchanging population or moving apart, respectively. Recently, an augmented FSSH (A-FSSH) algorithm has been proposed.48 Extra dynamical variables are introduced to characterize the width of the nuclear wave packet in position and momentum spaces. The variables are propagated together with the electronic wave function and the classical positions and momenta along each trajectory. They are used to obtain the decoherence rate and to yield a natural formalism for rescaling nuclear momenta following surface hops. A-FSSH has been tested in the dual avoided crossing and the extended coupling models suggested by Tully, as well as models with dumbbell and double arch geometries.48 In all these two level systems, A-FSSH achieves better performance than the standard FSSH, whereas the total computational cost is only a factor of two to four times higher. In addition, a slightly improved version of A-FSSH67 reproduces qualitatively the famous Marcus charge transfer rate58 for the spin-boson model.

A continuous strategy for decoherence eliminates the needs for stochastic sampling of decoherence events, thereby reducing the number of trajectories needed to achieve a convergence. A stochastic procedure is still needed to sample surface hops. The coherence penalty functional (CPF) approach49 eliminates the stochastic element completely, by introducing deterministic decoherence within the Ehrenfest dynamics. CPF maps the TDSE onto a fully classical Hamiltonian representation, using the Meyer–Miller–Thoss–Stock mapping.69 Decoherence is introduced by penalizing development of coherences using a CPF. The CPF is directly related to the fundamental formulation of decoherence introduced as a generalization of the standard, unitary quantum mechanics to the quantum mechanics of open systems by Lindblad.73 Although CPF is implemented at the mean field level, it is straightforward to combine CPF with surface hopping schemes because CPF merely uses a decoherence-corrected Hamiltonian for Ehrenfest dynamics. As demonstrated with Tully’s double avoided crossing model and the extended coupling with reflection model, as well as realistic electron transfer processes from Au and PbSe quantum dots into TiO2, the CPF method eliminates artificial interference and improves agreement with the fully quantum calculations and experiment.49 In a certain sense, CPF can be regarded as a counterpart of correlation functionals in DFT.

It has been realized early on35 that decoherence provides the physical mechanism for trajectory branching. Therefore, inclusion of decoherence effects eliminates the need for ad hoc surface hopping algorithms. Building upon this idea, decoherence-induced surface hopping (DISH)55 has been developed as an efficient surface hopping algorithm that uses standard quantum mechanics to obtain state populations, incorporates decoherence, and evolves nuclear trajectories on pure states. The method regards decoherence as a piece-wise continuous process.55 Together with the classical path approximation and the Ehrenfest method, DISH has been implemented in the publically available Pyxaid software for NA dynamics.75,76

Figure 2. (A) Diabatic potential energies and interstate coupling of Tully’s dual avoided crossing model, \(V_{11}(x) = 0, V_{22}(x) = -0.1\exp(-0.28x^2) + 0.05, V_{12}(x) = V_{21}(x) = 0.01\exp(-0.06x^2)\) in atomic units.22 (B) Reflection on state 1 obtained through exact quantum mechanics, standard FSSH,22 LS-FSSH,47 LS-GFSH, PC-FSSH,46 and SCMC47 in the adiabatic representation.
Trivial, “Unavoided” Crossings. When two diabatic states are symmetric and the system is modulated by only one continuous degree of freedom, the corresponding two adiabatic energy surfaces avoid each other. This noncrossing rule applies to diatomic molecules, where the bond length is the only parameter to tune the electronic structure. In more complex situations, all crossings are supposed to be “unavoided”. Each unavoidable crossing behaves as a double cone with a common vertex at the state degeneracy, and thus it is normally termed a conical intersection.76,77 However, the nuclear trajectory in surface hopping cannot explore the whole phase space. Effectively, the dynamics along the trajectory is one-dimensional, and the adiabatic PESs computed along the trajectory generally avoid each other. Crossings of noninteracting states constitute a very important exception because such crossings present an enormous numerical challenge in large systems. In these special cases, denoted as trivial crossings,8,39,50 the NA coupling approaches infinity at the exact crossing point and vanishes elsewhere else. Thereby, a trajectory must cross the intersection seam following the diabatic pathway. Mistreating trivial crossings may give rise to serious artifacts. For instance, in organic solids, only the neighboring molecules are coupled significantly, whereas non-nearest neighbors have negligible interaction with each other. A miss of a single trivial crossing in a numerical simulation will lead to an unphysically long-range population transfer.8,39,50 In recent years, trivial crossings have been dealt with using several strategies with distinct motivations.

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Because trivial crossings are qualitatively different from avoided crossings, one can identify them and treat accordingly. For this purpose, one can use a threshold for the energy gap between states or for the NA coupling magnitude.80 At the same time, finite time steps in numerical calculations can lead one to miss trivial crossings that are strongly localized in time. Trivial crossings can be detected through unphysical discontinuities in the PESs or the corresponding gradients;81 however, this scheme cannot be applied to Langevin dynamics or molecular dynamics at constant temperature. Recently, a Min-Cost algorithm has been proposed to efficiently track trivial, unavoidable crossings in time.38 A one-to-one correspondence is made between states at time $t$ and states at the following time step $t + \delta t$. This is achieved through maximizing the total squared overlap

$$\sum_\alpha s_{\alpha\alpha}^2(t; t + \delta t) \equiv \sum_\alpha \langle \phi_\alpha(t) | \phi_\alpha(t + \delta t) \rangle^2$$

(7)

where the $\alpha^{th}$ adiabatic state at time $t + \delta t$, $\phi_\alpha(t + \delta t)$, corresponds to the $\beta^{th}$ adiabatic state at time $t$, $\phi_\beta(t)$. If no reassignment is detected, avoided crossings dominate and normal surface hopping is used. Otherwise, unavoidable crossings are expected, and two situations may happen: If $s_{\alpha\alpha}(t)$ is lower than a critical value of $s_{\text{lim}}$, the crossing is treated by regular surface hopping. If $s_{\beta\beta}(t)$ is greater than $s_{\text{lim}}$, an avoided crossing between noninteracting states is detected, and the population of the $\beta$ state evaluated at $t$ is reassigned to the $\alpha$ state at $t + \delta t$ directly. Therefore, the active state is updated either according to hops predicted by surface hopping or based on unavoidable crossings detected by Min-Cost. This method has been implemented to investigate the energy transfer dynamics between two fragments of linear polyphenylene ethynylene chromophore units at various separations.82 It was shown that the Min-Cost algorithm can efficiently track the identity of states and detect unavoidable crossings. However, one may notice that this type of strategy uses a critical parameter to differentiate between avoided and trivial crossings. Therefore, it cannot describe cleanly intermediate crossings associated with weak interactions of different strengths. For instance, artificial energy transfer is still noticeable even between very weakly interacting fragments separated by 500 Å.38

The second strategy to deal with trivial crossings is to eliminate them from surface hopping simulations from the outset. This is possible because trivial crossings happen between adiabatic states that are far away in space. They give no contribution to quantum dynamics of localized charge carriers. To this end, a flexible surface hopping (FSH) technique has been proposed.30 FSH treats only a fraction of the system in a surface hopping manner and the remaining system with classical molecular dynamics. In line with quantum dynamics, FSH provides flexibility for the surface hopping subsystem, through adding or removing neighboring diabatic states to or from the subsystem. At each time step, every diabatic state, $|\psi_\alpha\rangle$, is picked out and forms a two-level system with the active state of the surface hopping subsystem, $|\psi_\beta\rangle$. When the absolute ratio between the corresponding electronic coupling and energy difference, $|\langle \phi_\beta | H | \phi_\alpha \rangle|/|\langle \phi_\beta | H | \phi_\beta \rangle⟩ - |\langle \phi_\alpha | H | \phi_\alpha \rangle⟩$, is larger than a critical fraction $R_c$, the state $|\psi_\beta\rangle$ is reserved to construct the new surface hopping subsystem. FSH bypasses the problematic trivial crossing problem because all adiabatic states in surface hopping are spatially close. The computational efficiency is increased because only a small Hamiltonian matrix requires diagonalization to get all important PES. FSH is especially suitable to deal with quantum dynamics in large molecular aggregates,19,50 in which electron couplings are extremely local in space. As an example, FSH has been applied to study charge transport in organic solids. With a Holstein–Peierls model, FSH is able to describe the crossover from a thermally activated hopping transport at low electronic coupling to a power law band-like temperature dependence at high couplings (see Figure 3A).30 This observation is confirmed by recent imaginary time path integral Monte Carlo simulations.82 The FSH study also provides a clear rational of the relationship between charge mobility and carrier size; in particular, it is found that the hopping-to-band crossover already occurs for charge carriers that spread over only a few molecular sites. It is also shown how thermal dynamic disorder can either decrease or enhance charge transport, depending on charge carrier localization (see Figure 3B). Note that the artificial long-range population transfer is completely prohibited in FSH.

Parameter-free surface hopping strategies to treat trivial crossings are also available. The adiabatic representation normally gives the most accurate results for surface hopping. However, a direct implementation of FSSH in the adiabatic representation needs an extremely small time interval to characterize trivial crossings in large systems. The widely adopted way to solve this problem is the local diabatization approach,58 in which one obtains the overlap between the adiabatic wave functions of adjacent time steps and transforms the adiabatic basis to a locally diabatic representation by Löwdin orthogonalization. A much simpler self-consistent FSSH (SC-FSSH) strategy was proposed in 2014.39 It provides a straightforward solution to the trivial crossing problem in surface hopping. In SC-FSSH, the wave function is propagated accurately in a diabatic or locally diabatic basis, and the
corresponding amplitudes in the preferred (e.g., adiabatic) basis are obtained through a representation transformation. During electronic dynamics, the total population is conserved; thus, the total surface hopping probability out of the active state \( g_{\text{tot}} \) is equal to the normalized population reduction in state \( a \)

\[
g_{\text{tot}} = \frac{\rho_{aa}(t) - \rho_{aa}(t + dt)}{\rho_{aa}(t)} 
\]

A self-consistency test failure violating eq 8 indicates that a trivial crossing problem is encountered. Trivial crossings happen between two adiabatic states with negligible energy difference; hence, the adiabatic state that gives the smallest energy difference with respect to the active state can be identified as the source of the problem. Then, the surface hopping probability to this state, \( g_{i} \), can be corrected as

\[
g_{i} = g_{\text{tot}} - \sum_{j \neq i} g_{j}
\]

Here, \( g_{\text{tot}} \) is the exact total surface hopping probability obtained through eq 8, and all \( g_{i} \) in the second term on the right band side are calculated with standard FSSH. This expression does not account for situations in which several trivial crossings occur within a single time step. However, such situations are rare and can be resolved by adopting a smaller time step. As demonstrated with the time-dependent electron population in the Holstein Hamiltonian, SC-FSSH gives enormous computational advantages. For a three-state example, it allows us to use a 200-fold larger time step than the standard FSSH. In the five-state case, the advantage is 10 000-fold! Even a large time step can give good results within SC-FSSH (see Figure 4).

**Super-Exchange and Representation Dependence.** Superexchange is a class of dynamical processes, where two electronic states are coupled indirectly through an intermediate state with a higher energy. In these cases, quantum population transfer proceeds through the intermediate virtual state, which is hardly populated. The first step of superexchange experiences a large energy barrier, and thus, hops to the intermediate state is classically forbidden in the standard FSSH, and the superexchange process cannot be described. The problem with superexchange arises in FSSH due to very strict rules on surface hopping probabilities and energy conservation. On the one hand, FSSH allows transitions only between states that are directly coupled. Second order transitions via virtual states, as in superexchange or Raman spectroscopy, are not possible. In this sense, FSSH can be regarded as a first-order theory. On the other hand, FSSH forces every surface hop to conserve the total quantum-classical energy. This feature is critical for attaining detailed balance between transitions up and down in energy, leading to thermodynamic equilibrium. At the same time, situations in which multiple surface hops can happen in a short period of time is not well described. Thus, the solution to this problem lies in modifying either the surface hopping probabilities, or the energy conservation processes, or both. The time derivative of population in each state is written in FSSH as a sum over contributions from hops to all other states, eq 4. This formalism ensures that surface hops follow population flux and the number of hops is minimized. However, this decomposition is far from unique. Suppose we have \( N \) states in the system, the number of fluxes between pairs of states is \( N(N - 1)/2 \). Solving the TDSE, one obtains changes in populations of all states. The population changes give rise to \( N \) linear equations to solve for the \( N(N - 1)/2 \) unknown state-to-state fluxes, or surface hopping rates. Recently, other strategies to define the flux have shown superior performance in dealing with superexchange.

Global flux surface hopping (GFSH) defines surface hopping probabilities based on the gross population flow between states rather than the state-to-state flux as in the standard FSSH. Except
The problem with superexchange arises in FSSH due to very strict rules on surface hopping probabilities and energy conservation.

for the different surface hopping probabilities, the other steps in GFSH are identical to FSSH. GFSH reduces to FSSH in the two state limit. In detail, one examines the population change of all states during a time step \([t, t + dt]\), \(\Delta \rho_i = \rho_i(t + dt) - \rho_i(t)\), and classifies the states into two subgroups: one with reduced population (group A) and the other with increased population (group B). Surface hops occur from states in group A to states in group B. The probability is proportional to the population decrease \(\Delta \rho_i\) and the population increase of the target state, \(\Delta \rho_j\). The GFSH transition probabilities are expressed as

\[
g_{ij} = \frac{\Delta \rho_j}{\rho_i} \frac{\Delta \rho_i}{\sum_{k \in A} \Delta \rho_{kk}} \quad (\text{if } i \in A \text{ and } j \in B) \tag{10}
\]

Note that the first ratio is similar to the expression shown on the last line of page 1064 in the FSSH paper, which takes a step further and obtains \(\Delta \rho_j^p\) to be explicitly proportional to the state-to-state couplings, eqs 4–6. Also note that similar expressions for transition probabilities have been suggested by Lisinetskaya and Mitríč when dealing with laser-induced coupled electron–nuclear dynamics. GFSH captures the superexchange mechanism of population transfer, whereas FSSH lacks this capability (see Figure 5). In other aspects, including minimization of the number of hops, internal consistency, velocity rescaling, and detailed balance, the GFSH algorithm is similar to FSSH. Besides the three-level superexchange model (Figure 5), the advantages of GFSH have been demonstrated with Auger processes in a realistic semiconductor quantum dot. Current studies indicate that GFSH can replace FSSH, but further tests are needed.

Starting from the pioneering works of Kramers and Anderson, the superexchange phenomenon is typically discussed in the framework of phenomenological models, employing diabatic representation. Manifestations of superexchange can be found in any representation. For instance, if donor and acceptor states in the diabatic representation are coupled via a series of high energy bridge sites, the corresponding adiabatic representation will exhibit a severe trivial crossing problem. The NA coupling between the two lowest adiabatic states, formed primarily by superpositions of the diabatic donor and acceptor states, will be very small until the adiabatic states cross in energy. The resulting avoiding crossing will be very sharp, the NA coupling will be extremely large, and simulations in the adiabatic representation will be very hard to perform numerically.

FSSH and other surface hopping schemes can be regarded as quantum master equations with rates derived from the TDSE. One can consider the surface hopping method from the viewpoint of a Markov state model, which assumes that future state probabilities depend only on the present state populations and not on the preceding sequence of events. Similarly to GFSH, Markov state surface hopping (MSSH) differs from the FSSH prescription only in the definition of the surface hopping probabilities. One may express the quantum populations at time \(t + dt\) as a linear expansion of the populations at time \(t\)

\[
\rho_j(t + dt) = \sum_i k_{ij}(t; t + dt)\rho_i(t) \tag{11}
\]

where \(k_{ij}(t; t + dt)\) describes the percentage of population transfer from state \(j\) to \(i\) during the time interval \([t, t + dt]\). It is straightforward to show that \(k_j(t; t + dt) = \rho_j(t + dt)\) is the solution. The transition probability from state \(j\) to state \(i\) is given by

\[
g_{ij} = \frac{k_{ij}}{\sum_i k_{ij}} \tag{12}
\]

which reduces to \(g_{ij} = \rho_i(t + dt)\). Thereby, MSSH defines the surface hopping probabilities as the quantum populations of the target states at the next time step. The resulting transition probabilities are the quantum state populations derived from the TDSE, just as in the original and mostly abandoned surface hopping approach of Tully and Preston, which is one of the
very first surface hopping algorithms. Recall that the method was replaced by FSSH because it produced excessive switching in extended regions of weak NA coupling. Similar to GFSH, the MSSH probability does not explicitly depend on the NA coupling between the source and target states and, thus, can potentially treat trivial crossings. The MSSH algorithm is surprisingly accurate when applied to superexchange modeling (see Figure 5). In addition, a modified dual avoided crossing model of Tully indicates that MSSH does not reduce to the mean field method and yields much better results, despite the strong resemblance with the mean field theory.51

\[ \text{GFSSH is as efficient as FSSH and can be realized simply by modifying the hopping probability formula.} \]

The standard Tully’s FSSH deals with population flow in Hilbert space. In comparison, standard quantum mechanics puts population and coherence on a more equal footing. With this motivation in mind, one can consider surface hopping in Liouville space. Quantum-classical Liouville equation has been known for some time.18,89 Solving it is a rather complex task that is achieved most commonly with ensembles of coupled trajectories.90 One can consider a simpler proposition of formulating FSSH type strategies by considering hopping of independent trajectories in Liouville space.25 To draw the analogy, one describes the quantum system using the density operator, \( \hat{\rho} \). For a pure state, it reads

\[ \hat{\rho}(t) = \langle \psi(t) \rangle \langle \psi(t) \rangle^\dagger \]  

The dynamics follows the quantum Liouville equation

\[ \frac{d\hat{\rho}(t)}{dt} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}] \]  

If we define

\[ \langle \rho \rangle = \sum_{ij} \rho_{ij} \langle ij \rangle \]

where, \( \langle ij \rangle \equiv \langle i \rangle \langle j \rangle \), eq 14 can be rewritten as

\[ \frac{d}{dt} \langle \rho \rangle = \frac{1}{i\hbar} \hat{L} \langle \rho \rangle \]  

Here, the superoperator \( \hat{L} \) connects all elements of \( \langle \rho \rangle \). Drawing upon the similarity between the Hilbert and Liouville formulations, eqs 1–2 and 15–16, we define the population of state \( \langle ij \rangle \) in Liouville space as \( \rho_{ij} \equiv \langle i \rangle \langle j \rangle \). Trpe\( \equiv 1 \) always holds for pure states; hence, \( \sum_{ij} \rho_{ij} = 1 \). \( \langle ij \rangle \rangle \) forms a complete, orthonormal basis for a quantum system in Liouville space, similar to \( \langle i \rangle \) in Hilbert space. By analogy, Liouville space FSSH (LS-FSSH) defines

\[ \frac{d\rho_{ij}}{dt} = \sum_{k \neq i \neq j} b_{ij,kl} \]  

where

\[ b_{ij,kl} = 2\hbar^{-1} \delta_{ik} \text{Im}[\rho_{ij}^\* (H - i\hbar \mathbf{d})_{kl}] \]

\[ + \delta_{lj} \text{Im}[\rho_{ij}^\* (H - i\hbar \mathbf{d})_{ki}] \]  

Similar to eq 6, the FSSH probability is given in Liouville space by

\[ g_{ij,kl} = -\frac{\Delta t_{ij,kl}}{p_{ij}} \]

In addition to the hopping probability, a surface hopping simulation requires state energies and the direction to define the component of the nuclear velocity to be rescaled. The energy of the coherence state, \( i \neq j \), is placed in the middle of the two corresponding Hilbert states.18,89 This is an approximate yet rational way to mimic the role of coherence in quantum dynamics.25 The velocity rescaling during a transition from state \( \langle ij \rangle \rangle \) to state \( \langle k,l \rangle \rangle \) is carried out along the direction of the sum of the NA coupling vectors \( \mathbf{d}_{ij} + \mathbf{d}_{kl} \). LS-FSSH holds the same level of internal consistency as standard FSSH in Hilbert space.25

Quantum interference is closely related to the phase difference between the nuclear wave packets evolving on different potential energy surfaces. In regions of strong NA coupling, the nuclei in
LS-FSSH tend to move on coherence surfaces, which locate in the middle of the two corresponding population surfaces. As a result, LS-FSSH provides a better treatment of the quantum phase and describes well quantum interference (see Figure 2). In addition, by explicitly correlating population states with coherence states, LS-FSSH is able to explore much more complex quantum mechanical pathways and reproduce the superexchange mechanism of population transfer (see Figure 5).

The simplest surface hopping recipes, including FSSH, represent nuclear wave packets by swarms of decoupled trajectories, which cannot exchange energy. By allowing energy exchange between different FSSH trajectories, one can model quantum tunneling and superexchange. This is achieved by the second-quantized surface hopping (SQUASH) algorithm. The space used in SQUASH is analogous to a many-particle basis in electronic structure theory. The evolution of each trajectory is independent of all other trajectories, as in FSSH. However, SQUASH permits energy flow between individual trajectories, mimicking closely the behavior of a quantum wave packet and introducing intrinsically quantum effects. Only the total energy of all trajectories is conserved. The method shows high efficiency and very accurate results for superexchange, improving greatly on the standard FSSH. SQUASH with two-trajectory states resembles LS-FSSH. Thereby, both methods obtain close results for the superexchange model (see Figure 5). SQUASH allows a more flexible description when more than two trajectories are coupled. In the terminology of LS-FSSH, such formulations would correspond to higher order tensors representing many-particle density matrices.

As discussed above, GFSH utilizes the gross population flow between states to derive surface hopping probabilities, and the Liouville space formulation of FSSH puts state populations and coherences on equal footing. Both ideas have shown superior results relative to the standard FSSH in Hilbert space. Liouville space GFSH (LS-GFSH) has been developed by merging the two ideas. The new method is nearly as straightforward as the standard FSSH, and carries comparable computational expense. Similar with LS-FSSH, LS-GFSH describe well the dual avoided crossing model with strong quantum interference (see Figure 2). LS-GFSH can also deal with trivial crossings because surface hopping probabilities do not rely explicitly on NA couplings. Tested with the representative superexchange model, LS-GFSH gives the best performance among all existing techniques in the FSSH series (see Figure 5). The obtained numerical results match almost perfectly the exact quantum mechanical solutions. Moreover, the results are nearly invariant under the choice of a basis state representation for surface hopping, for example, adiabatic vs diabatic, in contrast to the earlier techniques which exhibit notable basis set dependence. This property is particularly encouraging because exact quantum dynamics is representation independent. Note that the adopted one-dimension models, where the choice of direction for velocity rescaling is trivial, provide a perfect set of systems to study representation dependence of surface hopping. Because NA coupling is not computed in a diabatic representation, the velocity rescaling direction is not defined for diabatic representation in multiple dimensions. We suggest that one finds the direction along which the surface hopping probabilities are maximized. This more general principle is consistent with the standard rescaling along the NA coupling vector in the diabatic representation because changes in the diabatic state populations and surface hopping probabilities are largest when the classical subsystem evolves in the direction of the NA coupling vector. For higher dimensions, extensive studies in the diabatic representation are still lacking, and thus, the representation dependence deserves further investigation.

Outlook. The advantages of different surface hopping strategies for NA quantum dynamics are well known; however, the robustness of the surface hopping technique itself is essentially a black box. The reliability of surface hopping is normally based on the assumption that a nice performance with representative simple models also holds for realistic systems and complex processes. Starting from Tully’s seminal work in 1990, scattering models with two quantum levels and one classical degree of freedom have been widely adopted in the community. For instance, the dual avoided crossing model and the extended coupling with reflection model present a standard test suite for quantum interference and decoherence. Most surface hopping strategies are only tested against simple models of this type. To achieve a systematic assessment of the existing surface hopping methods and to lay the foundation for further theory developments, we need to expand substantially our benchmark base and to allow models to mimic all important features of quantum dynamics with tunneling, interference, decoherence, and superexchange effects mixed together. Especially models with multiple electronic states and multiple nuclear dimensions are extremely valuable. In recent years, studies on three levels or two classical degrees of freedom have been carried out, and the importance of superexchange and decoherence has been justified. Models with many nuclear degrees of freedom can mimic dissipation that is common in real systems and justify more rigorously simple decoherence corrections that assume rapid decoherence due to a combined effect of multiple nuclear modes.

If decoherence effects become important, we suggest DISH because it uses the standard quantum mechanical probability rules to determine hopping probabilities, avoiding ad hoc algorithms.

Exact quantum mechanical approaches provide benchmarks for the entire model base. However, a comprehensive assessment of all surface hopping strategies is not straightforward. Applying quantum mechanical standards to the models, one generates time-dependent populations of all electronic energy levels and nuclear wave functions to be compared to classical trajectories. By varying model parameters and initial conditions, huge amounts of data can be generated for comparison and analysis. Here, one should consider at least two major factors: accuracy and efficiency. Because large systems exhibit qualitatively different features that cannot be easily captured with small, exactly solvable models, it is also valuable to make comparison with time-resolved nonequilibrium experimental data. For example, large systems approach the thermodynamic limit, and thus, it is much more reasonable to describe loss of quantum coherence with a single Gaussian time scale. Excitation of one or two electrons from thousands of electrons present in nanoscale materials results in a small displacement of the nuclear coordinate equilibrium, for instance, compared to thermal nuclear fluctuations, justifying the classical path approximation.
It is also desirable to quantify the computational efficiency of various surface hopping techniques. Surface hopping simulations based on ab initio electronic structure methods are often limited by the computational expense of the electronic structure. In this case, convergence with respect to the numbers of trajectories becomes particularly important. The Ehrenfest method or the classical path approximation do not require sampling of the stochastic realization of the hopping process and, therefore, present a significant advantage. As the number of excited states involved in a surface hopping simulation increases, for example, in case of multiple excitons in semiconductor quantum dots, the surface hopping simulation itself becomes expensive, and special sampling techniques, or a sparse matrix representation of the active space, may be required. The balance between accuracy and efficiency is also very important. For small systems, accuracy is more valuable. However, with an increase of the system size, good efficiency with acceptable accuracy is highly demanded. A score matrix, or even a single ranking, may be defined based on validity, reliability, and applicability for a particular surface hopping strategy.

There exist dozens of surface hopping methods and variations. The methods are not universally accurate for all models and systems. A consideration of specifically designed models is necessary to reveal whether a surface hopping strategy is optimum for a given class of processes. A summary of this information would be quite helpful. New options in the surface hopping tool box are often developed to improve the performance of the standard FSSH in specific aspects. Thereby, an important task of the community is to determine whether there exists an ideal version of surface hopping that could resolve all limitations of FSSH and cover as many general situations as possible. Among the methods reviewed here, we would like to suggest GFSH might replace FSSH. GFSH is as efficient as FSSH and can be realized simply by modifying the hopping probability formula in exciting FSSH implementations. It produces similar accuracy for the standard problems and provides qualitative improvements for superexchange, electronic tunneling, and related phenomena. If decoherence effects become important, we suggest DISH because it uses the standard quantum mechanical probability rules to determine hopping probabilities, avoiding ad hoc algorithms, such as FSSH. We anticipate that DISH should be able to handle the superexchange phenomena.

As surface hopping is being applied to new classes of systems and processes, new ideas need to be introduced. This can be achieved through making proper approximations to the quantum-classical Liouville equation method, developed extensively by Kapral, Ciccotti, and co-workers. At the same time, full utilization of existing approaches is also indispensable. Especially, hybrid methods seem quite promising. LS-GFSH discussed above merges the concepts of Liouville space and global flux, producing a better performance than the parent LS-FSSH and GFSH methods when treating quantum interference, trivial crossings, superexchange, and representation dependence (see Figure 1). decoherence effects should be implemented within GFSH and the LS family of methods. By quenching populations of coherency states in LS-FSSH and LS-GFSH, decoherence will provide the mechanism for shifting all classical trajectories into population states, simplifying interpretation of the results. One could blend other surface hopping recipes, designed to resolve different limitations of FSSH. For instance, the ring polymer idea can be combined with other surface hopping methods to introduce nuclear quantum effects, such as tunneling and zero-point energy.

The phase-corrected Hamiltonian utilized in PC-FSSH can improve wave function propagation in various surface hopping strategies. Transition probability is the core for surface hopping. As shown above, there exist different formalisms with distinct motivations, including FSSH (and SC-FSSH), GFSH, and MSSH. Just as in exchange-correlation functionalities of density functional theory, one could possibly take a portion from each strategy and build an optimum combination to optimize performance in line with quantum solutions. Finally, an ideal surface hopping strategy should strive to satisfy general principles. Surface hopping populations should be consistent with quantum probabilities, that is, internally consistent. Hopping probabilities should satisfy detailed balance for transitions upward and downward in energy, leading to thermodynamic equilibrium. The results should be weakly dependent on representation, for example, adiabatic vs diabatic.

The progress in NA molecular dynamics simulations is driven by applications to novel systems and processes, which drive the development and implementation of innovative ideas and algorithms. Thorough exploration on a range of model problems is required to identify the difficulties and limitations of such methods and to find ways to improve them further. Such activities require a set of standardized and validated functional building blocks that can be mixed and matched together to explore novel ideas for performing accurate and efficient NA simulations. The functionality should be easy to work with, flexible, and transferable. Organized in this way, “methodology discovery” platforms can be created, to facilitate further developments of the approaches to NA dynamics. A hub of benchmark problems and validation techniques also are required. The source code should be open to the community to facilitate quality control and further extension. An effort in this direction has been initiated by one of the authors, resulting in the open-source “methodology discovery” library, named Libra. The code brings a wide functional that can be used in research problems and introduces an extensive educational material, showcasing the implementation of some of the approaches discussed above. This can be a valuable starting point for all students and postdoctoral researchers entering the field of NA simulations.

Excellent compatibility with modern electronic structure methods is one of the most significant advantages of surface hopping. Therefore, it is beneficial to develop methods for NA dynamics simulations and electronic structure calculations in parallel. An atomistic simulation of nonequilibrium dynamics in realistic applications relies on an accurate and efficient description of electronic structure. The density-functional tight-binding (DFTB) method has made great progress in recent years. DFTB and other semiempirical electronic structure methods significantly reduce the computational complexity while maintaining reasonable accuracy.
methodologies are much easier to implement than most of the electronic structure methods they are coupled with. We recommend that all graduate students working on NA molecular dynamics should be asked to write Ehrenfest and SSH codes at the beginning of their research. This experience can be greatly enhanced with the use of open-source methodology discovery and development platforms. Nevertheless, publically available and well-documented software tools are indispensable for popularizing the methodology and making it available to a broad scientific community. Recent developments in surface hopping and electronic structure allow scientists to address exceedingly more complex problems in physics, chemistry, biology, and material science.

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